# Simulation Study of the Link between Molecular Association and Reentrant Miscibility for a Mixture of Molecules with Directional Interactions

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The reentrant liquid-liquid miscibility of a symmetrical mixture with highly directional bonding interactions is studied by Gibbs ensemble Monte Carlo simulation. The resulting closed loop of immiscibility and the corresponding lower critical solution temperature are shown to be a direct consequence of the dramatic increase in association between unlike components as the temperature is lowered. Our exact calculations for an off-lattice system with a well-defined anisotropic potential confirm the findings of previous theoretical studies. [S0031-9007(99)09439-9]

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Reentrant phase behavior is one of the most characteristic and beguiling signatures of hydrogen bonding in simple and complex fluids alike. The so-called closed-loop liquid-liquid immiscibility found in a wide variety of fluid mixtures is a common example of the relationship between hydrogen-bonding association and reentrant behavior: here the region of liquid-liquid immiscibility is bounded above and below by upper and lower critical solution temperatures (UCST and LCST) (see Refs. [1,2] for general reviews). Closed-loop immiscibility was first reported for the nicotine-water mixture at the turn of the 20th Century [3]. Other well-known examples of this type of reentrant behavior include aqueous solutions of butan-2-ol [4], alkylpyridines [5], and alkylpolyoxyethylene nonionic surfactants [6], as well as a number of polymer solutions [7,8]. The common feature of these systems is the possibility of hydrogen bonding between the two components of the mixture. An increase in temperature overcomes the unfavorable enthalpic contribution (incompatibility of the two components) leading to miscibility above the UCST. The low-temperature miscibility below the LCST can be explained in terms of hydrogen bonding between unlike components which becomes the dominant feature of the free energy of the system, and results in a favorable heat of solution. One should note that in the case of polymer solutions the principal feature responsible for the LCST is the large difference in size between the polymer molecule and the solvent.

Hirshfelder *et al.* [9] were the first to suggest directional attractive forces as a direct cause of the LCST. This view is supported by the theoretical predictions of Barker and Fock [10], who analyzed a simple lattice model with interactions that depend on the relative orientations of the molecules using the Bethe-Guggenheim quasichemical approximation; an appropriate choice of parameters for the unlike directional interactions gives rise to closed-loop behavior. A more rigorous treatment of similar lattice models, using appropriate decoration transforma-

tions to the equivalent Ising models of ferromagnets [11] or alternatively using the Migdal-Kadanoff approximations of renormalization group (RG) theory [12], has also been applied to study closed-loop immiscibility in systems with highly asymmetrical interactions (e.g., see Refs. [13–18]). The results of the more recent calculations are in reasonable quantitative agreement with the asymmetric coexistence curves found in real systems, at least for pressures close to atmospheric. In addition to these analytical approaches, reentrant miscibility in similar lattice models has been studied with Monte Carlo techniques for both bulk [19] and confined systems [20]; as for the exact analytical studies, e.g., Refs. [13,15], symmetrical closed loops are seen, with the additional discovery of low-temperature self-assembled supermolecular structures. The lattice models are usually decorated lattices in which the different sides of the molecule are treated differently (directional) so that the contact energies of interaction with its neighbors depends on the relative orientation of the molecules. In all of these studies the reentrant behavior is a direct consequence of the directional interactions used to mimic hydrogen bonding.

It is clear from the ensuing discussion that most of the theoretical studies of closed-loop immiscibility have been within the framework of lattice models. Although the lattice approach provides the correct qualitative description of fluid phase behavior, the representation of the structure is a vast oversimplification. In most instances only nearest neighbor interactions are taken into account. Furthermore, the density of a lattice model is difficult to relate to that of a real fluid, and hence the pressure dependence of the phase equilibria is unrealistic. Continuum models on the other hand provide a more adequate description of a fluid. Various phenomenological continuum approaches have been used to study closed-loop immiscibility. Here, the highly anisotropic interactions are treated in terms of angle-averaged intermolecular potentials which have the appropriate temperature dependence. Reatto and Tau [21]

studied systems of spherical molecules with a temperature-dependent potential of mean force which includes solvent effects by accounting for the decrease in the size of the hydration shell as the temperature is increased; the mean spherical approximation was applied to describe the LCSTs of model micellar solutions. Goldstein [22] used a Flory-Huggins free energy expression together with a simple phenomenological term for the hydrogen-bonding interaction to describe closed-loop behavior in aqueous surfactant solutions. In fact an effective intermolecular interaction with the correct temperature dependence can always be found to reproduce reentrant behavior [23]. The problem with this type of phenomenological approach is that the exact form of the temperature dependence is unknown, and hence the description is merely qualitative and difficult to relate to a specific system.

An obvious alternative is to examine continuum models with well-defined directional attractive interactions. The Wertheim [24] approach offers an appropriate statistical mechanical framework to examine these associating systems. Such an approach has been used within an augmented van der Waals perturbation theory to describe closed-loop immiscibility in mixtures of molecules with directional attractive forces [2]: the model involves a symmetrical mixture of equal sized spherical molecules with unfavorable unlike mean-field interactions (which lead to liquid-liquid phase separation at moderate temperatures), and with additional directional bonding interactions between the unlike species (which leads to association and miscibility at low temperatures). This is essentially the first continuum study of closed-loop immiscibility for a system with a well-defined directional intermolecular potential. Although the preliminary theoretical study was for a rather unrealistic prototype system, the approach has been extended to provide a quantitative description of mixtures such as aqueous solutions of butanol, butoxyethanol, and alkylpolyoxyethylene nonionic surfactants [25,26]; it is particularly gratifying to find that the correct high-pressure behavior is predicted for these systems with these relatively simple continuum models.

Despite the large body of work in this area (the principal studies have already been mentioned), the link between association and the closed-loop behavior has not been explicitly shown for a specific model. In this Letter we present the results of Gibbs ensemble Monte Carlo simulation for the liquid-liquid phase equilibria of a symmetrical binary mixture with directional unlike attractive interactions, which is similar to the system studied theoretically in Ref. [2]. We aim to provide the first exact calculations of closed-loop immiscibility for an off-lattice system with a well-defined Hamiltonian. As well as confirming the results of the earlier theoretical findings, the focus of this paper is to show the direct unequivocal link between the association of the unlike species and the occurrence of the LCST. The simulation results of this prototype system should also provide a basis

for future studies of the LCST, such as the nature of the critical exponents and wetting behavior.

We study a symmetrical square-well binary mixture in which the unlike isotropic interaction is purely repulsive: the spherical core diameters $\sigma$ are equal ($\sigma = \sigma_{11} = \sigma_{12} = \sigma_{22}$), as are the ranges of the interactions ($\lambda = \lambda_{11} = \lambda_{12} = \lambda_{22} = 1.5$) and the well depths of the like interactions ($\varepsilon = \varepsilon_{11} = \varepsilon_{22}$), while the unlike well depth is zero ($\varepsilon_{12} = 0$). This system is seen to exhibit large regions of liquid-liquid immiscibility [27] due to the unfavorable interactions between unlike components. The inclusion of directional unlike attractions is necessary for the system to exhibit low-temperature miscibility. This is achieved by adding a single off-center and short-ranged square-well association site on each component to mimic the hydrogen-bonding interaction: the sites are placed halfway between the center and surface of the spherical core, have a range of $\lambda_{12}^{\mathrm{hb}} = 0.55$, a well depth of $\varepsilon_{12}^{\mathrm{hb}} = 14.5\varepsilon$, and only unlike site-site association is allowed.

The Gibbs ensemble Monte Carlo (GEMC) simulation technique [28,29] has become one of the most versatile methods to study phase equilibria in pure fluids and mixtures [30]. We use the standard GEMC technique in the isothermal-isobaric ensemble ($NPT$) as described in Ref. [27] although additional reorientational moves are now required. Because of the small volume of the site-site overlap region, large system sizes ($N = 1000$ and 1728, with equal numbers of both components) and long simulations ($\sim 2.5 \times 10^5$ GEMC cycles) are required to obtain good statistics.

A typical phase diagram for the model associating system is shown in Fig. 1(a) as a temperature-composition ($Tx$) isobaric slice. The closed-loop region of liquid-liquid immiscibility is clearly discernible; the system is totally miscible above a UCST ($T_c^* \sim 1.92$) and below an LCST ($T_c^* \sim 1.56$). It is clear from Fig. 1(a) that the system mixes below the LCST; the two boxes in the GEMC simulations become identical for temperatures slightly above the LCST. For larger values of the site-site energy $\varepsilon_{\mathrm{hb}}$, the unlike interactions are strong enough for the system to mix completely; in the case of smaller values of $\varepsilon_{\mathrm{hb}}$ the liquid-liquid immiscibility persists at lower temperatures [2]. An increase in the site-site interaction also increases the UCST, but the effect is less dramatic. Because of the symmetry of the intermolecular interactions, the phase diagram is symmetrical about a mole fraction of $x = \frac{1}{2}$: the densities and the degree of association of the two coexisting phases are equal while the mole fractions in the two phases are related by $x$ and $1 - x$. We define the degree of association in terms of $X_{\mathrm{hb}}$, the fraction of the total number of molecules which are bonded; two molecules are considered to be associated when the off-center bonding sites overlap. The fraction of molecules bonded in the coexisting phases is depicted in Fig. 1(b). Close to the UCST about 10% of the molecules are bonded. As expected the fraction of
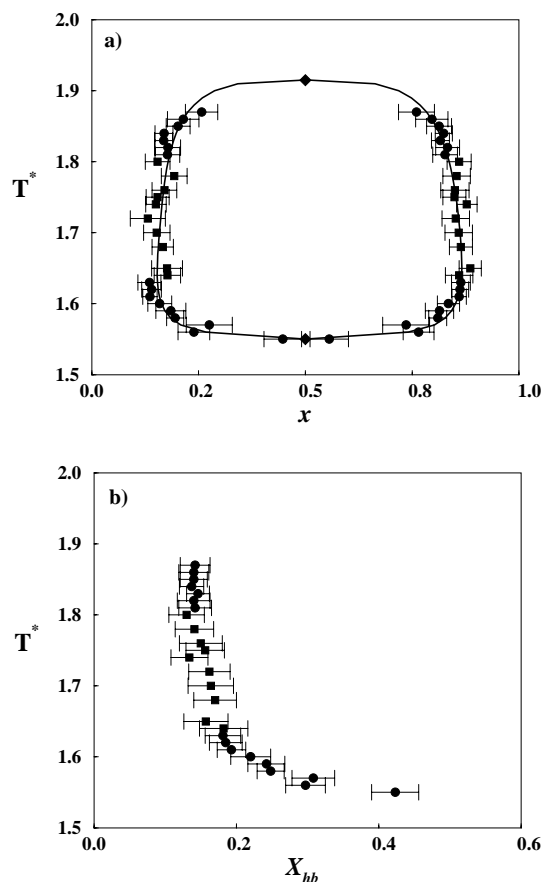
FIG. 1.   (a) The temperature-composition $(Tx)$ phase diagram for the symmetrical square-well mixture with unlike directional bonding interactions for a reduced pressure of $P^* = 1.28$ (where $T^* = kT/\varepsilon$ and $P^* = p\sigma^3/\varepsilon$). The data points correspond to Gibbs ensemble Monte Carlo simulations of the coexisting liquid phases for $N = 1000$ (squares) and 1728 (circles) particles, the estimated critical point (diamonds), and the solid curve is the Wegner fit to the simulation data. (b) The fraction of the total number of molecules bonded $X_{hb}$ as a function of temperature. The degree of association is shown for a single phase which, due to the symmetry of the interactions, is the same for both coexisting phases. The error bars correspond to one standard deviation.

molecules bonded increases with decreasing temperature. A dramatic increase in association is seen close to the LCST, where about 50% of the molecules are seen to be bonded. This clearly indicates that the LCST and subsequent miscibility occurs when a large proportion of the molecules is associated. The fraction of bonded molecules increases more slowly as the temperature is lowered below the LCST; the large change in association appears to be closely linked to the lower critical behavior.

One of the advantages of GEMC simulation is that it allows a description of phase equilibria moderately close to the critical point, at least until the critical fluctuations become larger than the box dimensions [31]. Simulations of finite systems in the canonical ensemble results in an overestimate of the critical temperature (or

an underestimate for an LCST). The results of GEMC simulations can be treated as "experimental data" and analyzed using the ideas of universal critical exponents and corrections to scaling [32]. The liquid-liquid phase transition exhibited by the square-well mixture belongs to the three-dimensional Ising-type universality class. Renormalization group theory leads to scaling laws for critical phenomena which can be used to correct for the behavior away from the asymptotic critical region [33]. The resulting expansion for the mole fraction can be written as an expansion in the departure from the critical temperature $t = 1 - T/T_c$ as [27,32]:

$$x_{\pm} = x_c + C_1|t|^{\psi} + C_2|t| + C_3|t|^{\psi+\Delta_1} + \cdots$$
$$\pm \frac{1}{2}(B_0|t|^{\beta} + B_1|t|^{\beta+\Delta_1} + B_2|t|^{\beta+2\Delta_1} + \cdots),$$
(1)

where $x_-$ and $x_+$ represent the two coexisting compositions, respectively, $x_c$ is the composition at the critical point, $C_i$ are coefficients in the expansion of the diameter of the coexistence curve, $\psi$ characterizes the anomaly in the diameter, $\Delta_1$ is a renormalization group gap exponent, $B_i$ are the correction amplitudes, and $\beta$ is the critical exponent.

In the case of our square-well mixture we take the universal critical exponent of $\beta = 0.325$, a RG gap exponent of $\Delta_1 = 0.5$, and include only the two leading terms $B_0$ and $B_1$ in the Wegner series to describe the liquid-liquid phase equilibria; the symmetry of the coexistence curve also means that $x_c = \frac{1}{2}$ and $C_2 = 0$ (since the diameters are parallel to the temperature axis). The series for the mole fraction of the system can thus be written as

$$x_{\pm} = \frac{1}{2} \pm \frac{1}{2}(B_0|t|^{\beta} + B_1|t|^{\beta+\Delta_1}).$$
(2)

The UCST and LCST can be analyzed with two separate series, and a full description of the closed loop can then be obtained by combining the two using a hyperbolic tangent switching function. The results of such a fit of the extended scaling series to the simulation data is shown as the solid curve in Fig. 1(a); the optimum values of the critical parameters are $T_c^* = 1.92$, $B_0 = 2.32$, and $B_1 = -2.61$ for the UCST and $T_c^* = 1.56$, $B_0 = 3.00$, and $B_1 = -4.15$ for the LCST. Clearly, our simple truncated Wegner series provides an adequate analytical description of the closed-loop envelope. Finite-size scaling (FSS) simulation techniques have recently been developed to properly describe the critical region; a full description can be found in the review by Allen [34]. We are currently undertaking a full FSS study of the LCST region to confirm universal critical behavior in this case.

In conclusion, we confirm that the low-temperature miscibility in systems with directional attractive interactions is a direct result of the sharp increase in association as the temperature approaches the LCST. It is important

to mention that, against the generally accepted view that closed-loop immiscibility and highly directional interactions are intricately linked, this type of phase behavior has been reported for Lennard-Jones molecules [35] and attractive spheres [36], where the attractive interactions are spherically symmetrical. These studies use approximate theories to describe the thermodynamics of the systems, and the corresponding LCSTs are found at extremely low temperatures for densities which are deep in the solid region. Although it is possible that isotropic interactions could give rise to reentrance under such unphysical conditions, anisotropic interactions such as hydrogen bonding are the central feature of systems which exhibit closed-loop behavior, a fact which is borne out by experiment. Here we have focused on liquid-liquid immiscibility of two phases with similar effective density which disappear at low temperatures. "Closed-loop" coexistence between phases of very different nature (e.g., vapor and liquid phases of different density) can be seen in nonassociating systems at high pressures and temperatures for systems with symmetrical interactions (see global phase behavior of Scott and van Konynenburg [37]). Reentrance can also be seen in charged-stabilized colloidal suspensions [38], which again is not caused by hydrogen bonding or molecular association; the complex interplay between Coulombic and entropic effects gives rise to the phase behavior.

Reentrant phase behavior is of course not restricted to simple fluids. Reentrant liquid crystalline nematic phases can be seen as a consequence of the delicate temperature dependence of hydrogen bonding (e.g., see Ref. [39]). In fact, molecular association and dipole pairing are often used to explain reentrant behavior [40]. Hydrogen bonding offers a number of new possibilities to control the phase transitions in liquid crystalline and polymeric systems.

[1] J. S. Walker and C. A. Vause, Sci. Am. **256**, 90 (1987).

[2] G. Jackson, Mol. Phys. **72**, 1365 (1991).

[3] C. S. Hudson, Z. Phys. Chem. **47**, 113 (1904).

[4] W. Dolgolenko, Z. Phys. Chem. **62**, 499 (1908).

[5] R. J. L. Andon and J. D. Cox, J. Chem. Soc. **1952**, 4601 (1952).

[6] J. C. Lang and R. D. Morgan, J. Chem. Phys. **73**, 5849 (1980).

[7] F. F. Nord, M. Bier, and S. N. Timasheff, J. Am. Chem. Soc. **73**, 289 (1951).

[8] G. N. Malcolm and J. S. Rowlinson, Trans. Faraday Soc. **53**, 921 (1957).

[9] J. Hirshfelder, D. Stevenson, and H. Eyring, J. Chem. Phys. **5**, 896 (1937).

[10] J. A. Barker and W. Fock, Discuss. Faraday Soc. **15**, 188 (1953).

[11] M. E. Fisher, Phys. Rev. **113**, 969 (1959).

[12] A. A. Migdal, Sov. Phys. JETP **42**, 743 (1976); L. P. Kadanoff, Ann. Phys. (N.Y.) **100**, 359 (1976).

[13] J. Wheeler, J. Chem. Phys. **62**, 433 (1975); J. Wheeler and G. R. Andersen, J. Chem. Phys. **69**, 2082 (1978); *ibid.* **69**, 3403 (1978); *ibid.* **73**, 5778 (1980).

[14] A. Robledo, Europhys. Lett. **1**, 303 (1986).

[15] J. S. Walker and C. A. Vause, Phys. Lett. **79A**, 421 (1980); *ibid.* **90A**, 419 (1982).

[16] R. E. Goldstein and J. S. Walker, J. Chem. Phys. **78**, 1492 (1983).

[17] J.-C. Lin and P. L. Taylor, Phys. Rev. Lett. **73**, 2863 (1994); Phys. Rev. E **49**, 2058 (1994).

[18] J.-M. Romero-Enrique, I. Rodriguez-Ponce, L. F. Rull, and U. Marini Bettolo Marconi, Mol. Phys. **93**, 501 (1998); Mol. Phys. **95**, 571 (1998); Phys. Rev. Lett. **79**, 3543 (1997).

[19] M. Kotelyanskii, B. Veytsman, and S. K. Kumar, Phys. Rev. E **58**, R12 (1998).

[20] M. Kotelyanskii and S. K. Kumar, Phys. Rev. Lett. **80**, 1252 (1998).

[21] L. Reatto and M. Tau, Chem. Phys. Lett. **108**, 292 (1984).

[22] R. E. Goldstein, J. Chem. Phys. **84**, 3367 (1986).

[23] M. Gencaslan, P. H. E. Meijer, M. Keskin, and A. H. L. Levelt, J. Supercrit. Fluids **7**, 107 (1994).

[24] M. S. Wertheim, J. Stat. Phys. **35**, 19 (1984); *ibid.* **35**, 35 (1984); *ibid.* **42**, 459 (1986); *ibid.* **42**, 477 (1986).

[25] M. N. Garcia-Lisbona, A. Galindo, G. Jackson, and A. Burgess, Mol. Phys. **93**, 57 (1998).

[26] M. N. Garcia-Lisbona, A. Galindo, G. Jackson, and A. Burgess, J. Am. Chem. Soc. **120**, 4191 (1998).

[27] D. G. Green, G. Jackson, E. de Miguel, and L. F. Rull, J. Chem. Phys. **101**, 3190 (1994).

[28] A. Z. Panagiotopoulos, Mol. Phys. **61**, 813 (1987).

[29] A. Z. Panagiotopoulos, N. Quirke, M. R. Stapelton, and D. J. Tildesley, Mol. Phys. **63**, 527 (1988).

[30] K. E. Gubbins, Mol. Simul. **2**, 223 (1989); A. Z. Panagiotopoulos, Mol. Simul. **9**, 1 (1992).

[31] B. Smit, Ph. de Smedt, and D. Frenkel, Mol. Phys. **68**, 931 (1989).

[32] J. V. Sengers and J. M. H. Levelt Sengers, Annu. Rev. Phys. Chem. **37**, 189 (1986).

[33] F. J. Wegner, Phys. Rev. B **5**, 4529 (1972).

[34] M. P. Allen, *Computer Simulation in Chemical Physics,* edited by M. P. Allen and D. J. Tildesley (Kluwer Academic, New York, 1993), pp. 49–92.

[35] V. A. Mazur, L. Z. Boshkov, and V. B. Fedorov, Dokl. Akad. Nauk SSSR **282**, 137 (1985); L. Z. Boshkov and V. A. Mazur, Russ. J. Phys. Chem. **60**, 16 (1986); L. Z. Boshkov, Dokl. Akad. Nauk SSSR **294**, 901 (1987).

[36] L. V. Yelash and T. Kraska, Ber. Bunsen-Ges. Phys. Chem. **102**, 213 (1998).

[37] R. L. Scott and P. H. van Konynenburg, Discuss. Faraday Soc. **49**, 87 (1970).

[38] R. van Roij, M. Dijkstra, and J.-P. Hansen, Phys. Rev. E **59**, 2010 (1999).

[39] R. P. Sear and G. Jackson, Mol. Phys. **83**, 961 (1994); Phys. Rev. Lett. **74**, 4261 (1995).

[40] P. E. Cladis, Mol. Cryst. Liq. Cryst. **85**, 165 (1988).